

## SAC-CI

This keyword requests SAC and SAC-CI calculations [1,2]. SAC calculates symmetry-adapted cluster expansion for singlet closed-shell (ground) state [3] and SAC-CI calculates open-shell singlet excited states, triplet ground and excited states, doublet ionized and doublet electron-attached ground and excited states [4], and from quartet to septet [5] ground and excited states. SAC is always necessary for SAC-CI calculations. The SAC wave function is expressed as

$$|\Psi^{\text{SAC}}\rangle = \exp\left(\sum_{I=1}^M C_I S_I\right) |\Phi_0\rangle,$$

with a closed-shell determinant  $\Phi_0$ , which is usually Hartree-Fock, and the SAC-CI wave functions are expressed using the SAC wave function as

$$|\Psi^{\text{SAC-CI}}\rangle = \sum_{K=0}^N d_K R_K |\Psi^{\text{SAC}}\rangle,$$

where  $S_I$  for SAC and  $R_K$  for SAC-CI are symmetry-adapted excitation operators,  $R_0 = 1$ , and  $C_I$  and  $d_K$  are variable coefficients. The SAC-CI SD(single double)-R method is appropriate for ordinary single-electron excitation, ionization, and electron-attachment processes and the SAC-CI general-R method [6], in which the SAC-CI excitation operators  $\{R_K\}$  are composed of single to sextuple excitations, is appropriate for multi-electron processes like two-electron excited states and shake-up ionizations [7]. Perturbation selection is done for the linked operators higher than doubles to reduce computational labor. For molecules having degeneracy, the perturbation selection is done so as to keep the degeneracy. When you calculate a property over different geometries (e.g. potential energy curve), you must take a group-sum of the selected operators over the geometries (see GSUM below), since otherwise the property may be calculated discontinuously. Energy gradient method is available for all the states calculated by the SAC and SAC-CI SD-R method [8], general-R method [9] and high-spin multiplet method [10]. Geometry optimization is possible with a keyword OPT. Detailed explanations and usage of the SAC/SAC-CI program in GAUSSIAN are given in the GUIDE in the present SAC-CI homepage [2]. Note that the so-called EOM-CC and CCLRT methods are theoretically equivalent [2,7] to the SAC-CI method published much earlier.

### REFERENCE MO, ACTIVE SPACE, AND INTEGRAL TRANSFORMATION:

SAC/SAC-CI usually uses closed-shell restricted Hartree-Fock (RHF) MO as reference orbital, but restricted open-shell Hartree-Fock (ROHF) MO, MC-SCF MO, etc. can also be used as reference MO when such SCF is performed before the SAC/SAC-CI step. But unrestricted Hartree-Fock (UHF) MO is rejected. Localized (L) MO can be used by doing localization just before the integral transformation. The spin multiplicity and molecular charge used in the SCF step are modified when they are specified in the SAC/SAC-CI step. For gradient calculations and geometry optimizations, only closed-shell RHF MOs are adaptable to the SAC/SAC-CI part.

Rydberg bases are important for studying excited states, in particular, Rydberg excited states. Size of active space is important for the quality of SAC-CI calculations: we recommend to use all-valence active space including Rydberg orbitals (default for active space).

Electron repulsion integrals (ERIs) are transformed within the specified active orbital space and stored in the 'in-core memory' for fast random access in calculating integrals. Zero integrals by symmetry are not stored. To achieve good performance of SAC/SAC-CI, we recommend to use appropriate memory size of your computer with **%mem**. For large systems, the storage of ERIs usually dominates the memory and when the space of ERIs exceeds the memory size, the SAC-CI calculations are done with ERIs separately allocated in memory and disc.

**Direct** requests to use the direct algorithm for the SAC/SAC-CI SD-R calculations. **Direct** is not compatible with **General-R**, **WithoutR2S2**, **FullUnLinked**, **InCoreDiag**, and **InCoreSAC**. The direct SAC-CI code uses different values of internal thresholds, which correspond to the conventional SAC-CI calculations with **NoUnlinkedSelection** keywords. Therefore, the results obtained with the direct SAC-CI code are usually different from the results with the conventional SAC-CI code. The direct SAC-CI code is efficient and therefore, strongly recommended. (G09.B01 and later) [11]

Direct SAC-CI SD-R LevelThree calculation for singlet states of C<sub>2v</sub> molecule with double-zeta basis.

```
#SAC-CI(Direct, Singlet=(Nstate=(2,1,3,2)))
/D95 Pop=Full
```

**LMO = item** requests to use localized MO as reference orbital. Pipek-Mezey LMO (**PM** or **Pipek-Mezy**) is recommended. Boys LMO (**Boys**) is also available.

**FC (default)** is a synonym of **FrozenCore** and implies that inner-shells are excluded from the active space of the SAC/SAC-CI calculations.

**FullActive** includes all SCF MOs in the active space, and is a synonym of **Full**.

**Window = (M, [N])** is a synonym of **ReadWindow = (M, [N])** and means that the SAC/SAC-CI calculation is done within the *M*-th to *N*-th active orbital space (*M* < *N* in the energy order).

# For calculations of ESR hfs constants, 1s-core MO should be included in the active space.

**CorePrWindow=(m, n)** activates the calculation of core-excited/core-ionized states and specifies core orbitals from which an electron is excited or ionized in the core-electron processes; *m* and *n* specifies the range of core orbitals. This keyword is used with the **FullActive** or **Window** keyword to include core-orbitals in the active space. (G09.C01 and later)

Direct SAC-CI SD-R calculation of singlet O1s excited states of CO. (See test966)

```
#SAC-CI(Direct, Singlets=(Nstate=(0,0,1,0),
      FullActive,CorePrWindow=(1,1))
/cc-pVTZ Pop=Full
```

### SAC/SAC-CI KEYWORDS:

SAC-CI **SD-R** calculation may be started with the option **SelecCISonly** to examine the states to be calculated, and at the same time, the size of the calculation (number of linked operators) may be checked with the options **LevelOne/LevelTwo/LevelThree**. Then, full SAC/SAC-CI calculations are performed using the options given below. Afterwards, the accuracy of the results may be checked by using different basis set and higher Level-options. For multi-electron processes, SAC-CI **General-R** method is more accurate than the **SD-R** method.

### ACCURACY

**SD-R** calculates within singles and doubles linked excitation operators (default).

**General-R** includes up to sextuple linked excitation operators [6,7].

### **LevelOne/LevelTwo/LevelThree**

thresholds of the perturbation selection of the linked double-excitation operators for SAC/SAC-CI are in levels one, two, and three in increasing accuracy. LevelThree is default. (In LevelOne, EThreS2=1\*10<sup>-5</sup>, EThreR2=1\*10<sup>-6</sup>, in LevelTwo, EThreS2=5\*10<sup>-6</sup>, EThreR2=5\*10<sup>-7</sup>, and in LevelThree, EThreS2=1\*10<sup>-6</sup>, EThreR2=1\*10<sup>-7</sup>)

**NoLinkedSelection** suppresses perturbation selection for linked operators.

**WithoutDegeneracy** for degenerate molecules, the perturbation selection in the SD-R calculation is done so as to keep the degeneracy (default), but with this option this special care is made off, for reducing computational time (non-default).

**WithoutR2S2** ignores R2S2-type unlinked integrals in SAC-CI calculations. This is effective for reducing computational time of SAC-CI SD-R calculations, though the results are somewhat affected.

### **NoUnLinkedSelection**

suppresses the selection for unlinked operators adopted currently.

**FullUnlinked** forces to include all types of unlinked terms. All the linked and unlinked terms are included without selection and the SAC-CI is forced to be solved with in-core algorithm.

**EgOp** requests to generate higher-order (more-than-triple) linked operators in general-R by the exponential generation algorithm (default for single point energy calculation). The highest R is specified by **MaxR** ( $\leq 6$ ). Then, perturbation selection is done with the thresholds that are the same as those for EThreS2 in LevelOne/LevelTwo/LevelThree.

**FullRGeneration** requests to generate all higher-order linked operators in general-R with **MaxR**  $\leq 4$  and then to perform perturbation selection as above. (**EgOp** is usually default in general-R, but this is default for gradient calculations and geometry

optimizations.)

## SPIN STATE

**Singlet** = *spin-state-specific sub-keywords*

specifies **singlet** states calculations.

You can also calculate the following spin states.

**CationDoublet** (a synonym of **Doublet**)

**AnionDoublet**

**Triplet**

**Quartet**

**Quintet**

**Sextet**

**Septet**

# For doublet states, see also **AddElectron** and **SubElectron** options below.

## SPIN-STATE-SPECIFIC SUB-KEYWORDS

**NState** = (*N1*,...,*N8*) sets the number of states *N1*,...,*N8* to be calculated by the SAC-CI method for each irreducible representation 1,...,8 of the point group of the molecule.

**NState** = *N* means **NState** = (*N*,*N*,...).

# SAC state is always calculated and not included in *N*.

# *Nk* most stable states of *k*-symmetry are selected from the SECI result in SD-R SAC-CI and from the SDCI result in general-R SAC-CI.

# Number of irreducible representation is eight for  $D_{2h}$ , which is maximum in abelian group. For  $C_{2v}$ , four integers can be specified as **NState** = (*N1*,*N2*,*N3*,*N4*).

# For degenerate symmetry, the SAC-CI calculation is done in a closest linear symmetry ( $D_2$  for  $T_d$ , for example) and **NState** option is given for this linear symmetry (**NState**=(1,2,0,0) for calculating one  $A_1$  (or E) and two T states of  $T_d$  symmetry). The closest linear symmetry used in default for degenerate symmetry is summarized in SAC-CI Guide [2]. See also **WithoutDegeneracy** option.

# You may decide the number of solutions referring to the CIS vectors calculated beforehand of SAC-CI (see keyword **SelecCISonly**.)

**MaxR** = *N* sets the maximum excitation level, *N*, ( $N \leq 6$  for **EgOp**,  $N \leq 4$  for **FullRGeneration**) of the linked excitation operators in general-R.

**Variational** solves the SAC-CI equation by diagonalizing symmetrized matrices. (default)

**NonVariational** solves the SAC-CI equation for non-symmetric matrices. Note that SAC is always solved 'non-variationally'.

**InCoreDiag** forces to solve SAC-CI using in-core algorithms.

**Iterative** = *item* forces to solve SAC and SAC-CI using iterative algorithms. *Item* specifies

initial guess: **SInitial** sets CIS solution and **SDInitial** (default) sets CISD solution as initial guess.

**Density** requests to calculate density matrices, together with Mulliken population, charge, dipole moment and second moment, for the SAC/SAC-CI states calculated. For other properties, see the whole-state keywords, **AllProperties** and **NoProperty** given below.

**SpinDensity** requests to calculate spin density matrices. Note that this keyword activates the keyword **FullActive**.

**TransitionDensity/NoTransitionDensity** requests (default) / suppresses calculations of transition density and oscillator strength between SAC ground state and SAC-CI singlet excited states. For other spin-symmetries, the transition density is calculated in default between the lowest SAC-CI state and SAC-CI excited states. (See also **TransitionFrom**).

SAC-CI SD-R LevelThree calculation for singlet, triplet, and ionized states of  $C_{2v}$  molecule with double-zeta basis.

```
#SAC-CI(Singlet=(Nstate=(2,1,3,2)),  
        Triplet=(Nstate=(2,1,3,2)),  
        CationDoublet=(Nstate=(3,0,2,3)))  
/D95 Pop=Full
```

SAC-CI general-R LevelTwo calculation of the ionized states of a molecule in  $D_2$  symmetry with the R-operators up to quadruples within the active space of the second to 14-th MOs.

```
#SAC-CI(Window=(2,14), LevelTwo, General-R,  
        CationDoublet=(Nstate=(3,0,1,1), MaxR=4))  
/D95
```

## GRADIENT CALCULATION AND GEOMETRY OPTIMIZATION

**TargetState = (SpinState=*Spin*, Symmetry=*M*, Root=*N*)**

specifies the target state for which the gradient calculation or geometry optimization is done. The following three items must be specified. *Spin* specifies the spin multiplicity of the target state using one of **Singlet**, **CationDoublet**, **AnionDoublet**, **Triplet**, **Quartet**, **Quintet**, **Sextet**, and **Septet**. *M* specifies the irreducible representation number of the point group, which is defined in the SCF step. *N* specifies the solution number in the desired *Spin-Symmetry* state.

# To fix these parameters, we recommend to perform single point SAC-CI calculation before doing the geometry optimization.

# When the SAC solution is your target, specify as

**TargetState = (SpinState=Singlet, Symmetry=1, Root=0).**

# In general-R, the generation of the higher-order linked operators is

automatically forced to be **FullRGeneration** for gradient calculations and geometry optimizations.

**MacroIteration = N** ( $N \leq 3$ )

requests to iterate macro optimization step N-times. MacroIteration=1 is default.

An additional single-point SAC-CI calculation is done after optimization using the optimized geometry.

#### RELATED KEYWORDS

**CPHF = Canonical** means that derivatives are evaluated by differentiating the canonical MO set.

**CPHF = MOD** (default)

means that the derivatives are evaluated by differentiating the minimum orbital deformation (MOD) [12,13] condition to avoid singularities in the energy gradient calculations. See **CPHF**.

**Force** activates gradient calculation.

**Opt** activates geometry optimization.

# **Freq** does not work in the SAC and SAC-CI calculations.

Geometry optimization for the second triplet B1 excited state of  $C_{2v}$  molecule.

```
#SAC-CI=(Triplet=(NState=(0,0,2,0)),  
          TargetState=(SpinState=Triplet, Symmetry=3, Root=2))  
/D95* Opt
```

#### ODD-ELECTRON MOLECULE AND ROHF ORBITAL

When your target is odd-electron molecule and the SCF procedure is carried out with odd number of electrons, an even-electron closed-shell configuration must be constructed for the SAC method, since SAC is for closed-shell in this program. The following two options are available to modify the open-shell SCF configuration into a closed-shell configuration.

**AddElectron** requests to add one electron to the open-shell SCF configuration. This is a default action when **CationDoublet**, **Quartet**, and **Sextet** are treated.

**SubElectron** requests to subtract one electron from the open-shell SCF configuration. This is a default action when **AnionDoublet** is treated.

ROHF MOs of neutral radical may be used and the SAC calculation is done for closed-shell anion (cation), and the ground and excited states of the neutral radical is solved by the SAC-CI method with **CationDoublet** (**AnionDoublet**) option.

```
#SAC-CI(AddElectron, CationDoublet=(NState=(2,1,2,3)))  
/D95 ROHF
```

```
#SAC-CI(SubElectron, AnionDoublet=(NState=(2,1,2,3)))  
/D95 ROHF
```

## ITERATIVE METHOD

- InCoreSAC** forces to solve SAC using in-core algorithms.
- MaxItDiag** =  $N$  sets maximum number of iterations to  $N$  for diagonalization.
- MaxItSAC** =  $N$  sets maximum number of iterations to  $N$  in solving SAC equation.
- DConvDiag** =  $M$  sets the energy convergence criterion to  $10^{-M}$  in the diagonalizations for SAC-CI and CI.
- DConvSAC** =  $M$  sets the energy convergence criterion to  $10^{-M}$  in solving SAC equation

## DENSITY AND TRANSITION DENSITY

- TransitionFrom** = (**SpinState**= $Spin$ , **Symmetry**= $M$ , **Root**= $N$ ) specifies the initial state for calculating transition density matrices.  $Spin$ ,  $M$  and  $N$  work in the same manner as the options in **TargetState**. All states of the same spin-space symmetry calculated are used as the final states.
- AllProperties** requests to calculate all multipole moments up to hexadecapole, all  $N$ -th moment up to fourth-moment, all electrostatic properties, and diamagnetic terms (shielding and susceptibility). This option works for all spin-states for which **Density** is specified.
- NoProperty** suppresses the calculations of any properties.

## GSUM (GROUP SUM OF SELECTED OPERATORS)

When molecular properties are studied over different geometries using perturbation selection, we must take a group-sum (GSUM) of the linked and unlinked operators selected at different geometries, since otherwise the properties may be calculated discontinuously.

- BeforeGSUM** requests to initialize a series of GSUM calculations. This keyword must be used at the first geometry of the GSUM calculations.
- CalcGSUM** requests to add the operators selected at current geometry to the group-sum (GSUM) set.
- AfterGSUM** requests to perform SAC/SAC-CI calculations using the GSUM operators collected at all geometries.
- # In **CalcGSUM**, the SCF orbitals are re-ordered to be the same, in nature, as the former orbital sequence. This re-ordering is carried out automatically in Link 801.
- # The same symmetry point group must be used in all GSUM calculations.
- # **BGSUM**, **CGSUM**, and **AGSUM** are synonyms of the above keywords.
- # GSUM is available only for SAC/SAC-CI SD-R calculations of singlet, triplet, ionized, and electron-attached states, not for general-R and high-spin states.
- # In a series of GSUM calculations, the minimum orbital deformation (MOD) condition is satisfied automatically.
- # For more details, see GUIDE [2].

Potential energy curves of the singlet excited states of a linear homonuclear molecule are calculated by the GSUM options with canonical orbitals using in-core algorithm.

```
%Chk=Mol
#SAC-CI(BeforeGSUM,Singlet=(NState=(1,0,1,0,0,1,1,0),
      InCoreDiag))
      /D95(d) Unit=Bohr CPHF=Canonical

Start GSUM at R=4.0 au.

0 1
Li
Li 1 4.00

--Link1--

%Chk=Mol
#SAC-CI(CalcGSUM,Singlet=(NState=(1,0,1,0,0,1,1,0),InCoreDiag))
      /D95(d) SCAN Unit=Bohr CPHF=Canonical

Calc. GSUM from R=5.0 to R=12.0 au.

0 1
Li
Li 1 R1

R1 5.0 7 1.0

--Link1--

%Chk=Mol
#SAC-CI(AfterGSUM,Singlet=(NState=(1,0,1,0,0,1,1,0),InCoreDiag))
      /D95(d) SCAN Unit=Bohr CPHF=Canonical

After GSUM back from R=12.0 to R=4.0 au.

0 1
Li
Li 1 R1

R1 12.0 8 -1.0
```

## MEMORY REQUIREMENT

**MaxR2Op** =  $N$  sets maximum number of R2 operators after perturbation selection to  $N$ .  
The default number is 100000.

**MaxEgOp** =  $N$  sets maximum number of operators in general-R method to  $N$ . The default  
number is 5000.

## OTHERS

**SelecCISonly** forces to stop the process after CIS and perturbation selection. The CIS vectors and the numbers of the selected linked-excitation operators are printed out. For SAC-CI calculations of ordinary one-electron excited, ionized, and electron attached states, the target states and the corresponding dimensions of the linked excitation operators are examined using this Keyword before doing full SAC-CI calculations.

**SACOnly** performs only the SAC calculation and does not compute any excited states.

### MORE INFORMATION

Instructive sample inputs and the scientific presentations of the calculated results are given in the SAC/SAC-CI Guide attached at the top of Link 923 [2], together with the detailed explanations of the SAC/SAC-CI method and the algorithms currently adopted. The outputs for the sample inputs are given in the directory g09/tests/.

### References

- (1) H. Nakatsuji, in Computational Chemistry - Reviews of Current Trends, Vol. 2, ed. J. Leszczynski, World Scientific, 1997, pp.62-124.
- (2) SAC/SAC-CI GUIDE, in the present SAC-CI homepage.
- (3) H. Nakatsuji and K. Hirao, J. Chem. Phys. 68, 2053 (1978).
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- (6) H. Nakatsuji, Chem. Phys. Lett. 177, 331 (1991); J. Chem. Phys. 94, 6716 (1991).
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- (9) M. Ishida, K. Toyota, M. Ehara, and H. Nakatsuji, Chem. Phys. Lett. 347, 493 (2001).
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- (13) K. Toyota, M. Ishida, M. Ehara, M.J. Frisch, H. Nakatsuji, 367, 730 (2003).